

## CHAPTER 4

### 4. MO CALCULATIONS OF UREA MONOMERS AND DIMERS

In order to check the validity of approximations necessary to simplify cluster calculations, we performed a series of calculations on urea and thiourea monomers and dimers at different levels of the theory.

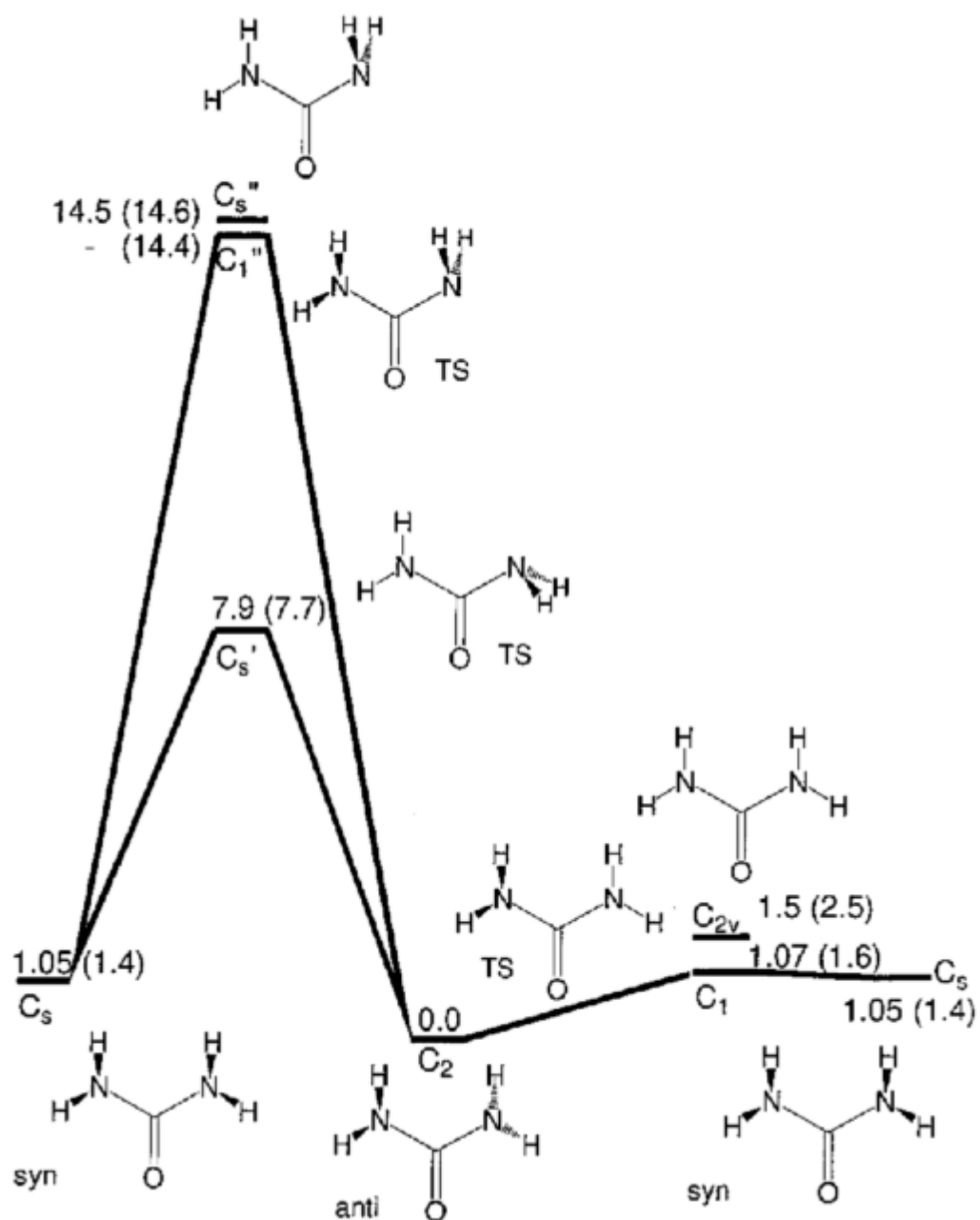
*Ab initio* (HF, MP2 and B3W91 with basis sets up to D95++\*\*) and semiempirical (AM1, PM3 and SAM1) molecular orbital calculations are presented in this Chapter for urea and four different general classes of urea dimeric structures that correspond to interactions between the nearest neighbor molecular pairs in the crystal structures of urea and thiourea. While the urea monomers have nonplanar minima on all *ab initio* surfaces, on the HF and MP2/6-311+G (3df,2p) surfaces they are planar after vibrational and thermal corrections. Urea chain and ribbon dimers are calculated to be planar after counterpoise and thermal corrections for all HF calculations and nonplanar for MP2 calculations (D95\*\* and D95++\*\*). The DFT calculations predict planar chain, but nonplanar ribbon dimers. The ribbon dimer is the most stable, as it uses both H-bond acceptors, while the chain dimer uses only one, and the herring-bone dimer has one H-bond. Stacking interaction is much less stabilizing, and does not correspond to the energy minimum. The PM3 method fails in both predicting molecular conformations and H-bonds while AM1 gives reasonable results.

#### 4.1 Molecular conformations and transition states of urea

The results for the urea monomer are summarized in Tables 4.1-4.4. Figure 4.1

**Table 4.1.** Results of semiempirical and *ab initio* calculations for urea transition states and conformers. NI - number of imaginary frequencies;  $\Delta H_0$  - heat of formation (kcal/mol); E - total electronic energy (a.u.);  $\Delta E$  - relative energy (kcal/mol);  $\Delta\Delta H_0$  - relative energy with zero point vibration correction (kcal/mol);  $\Delta\Delta H_{298}$  - relative energy corrected for thermal vibrations at 298K (kcal/mol).

Method	Symmetry	NI	$\Delta H_0$	E	$\Delta E$	$\Delta\Delta H_0$	$\Delta\Delta H_{298}$
AM1	$C_{2v}$	1	-44.08				0.87
	$C_2$	0	-44.95				0.00
	$C_s'$	1	-40.22				4.73
	$C_s''$	1	-36.32				8.63
SAM1	$C_{2v}$	1	-44.07				0.04
	$C_2$	0	-44.11				0.00
	$C_s'$	1	-37.86				6.25
	$C_s''$	1	-33.02				11.09
PM3	$C_{2v}$	2	-40.96				6.05
	$C_2$	0	-47.01				0.00
	$C_s$	0	-45.82				1.19
	$C_1$	1	-44.10				2.91
	$C_s'$	2	-42.38				4.63
	$C_s''$	2	-37.35				9.66
	$C_1'$	1	-43.55				3.46
	$C_1''$	1	-39.37				7.64
HF/D95**	$C_{2v}$	2		-224.046152	1.29	0.00	0.00
	$C_2$	0		-224.048215	0.00	0.14	0.37
	$C_s$	0		-224.046551	1.04	0.35	1.05
	$C_1$	1		-224.046550	1.04	0.25	0.46
	$C_s'$	1		-224.034185	8.80	8.38	8.50
	$C_s''$	2		-224.023599	15.45	14.26	13.76
	$C_1''$	1		-224.023616	15.44	14.50	14.28
MP2/D95**	$C_{2v}$	2		-224.681770	2.49	1.04	0.84
	$C_2$	0		-224.685742	0.00	0.00	0.00
	$C_s$	0		-224.683453	1.44	1.01	1.20
	$C_1$	1		-224.683216	1.59	0.78	0.71
	$C_s'$	1		-224.673522	7.67	6.86	6.82
	$C_s''$	2		-224.662535	14.56	13.13	12.76
	$C_1''$	1		-224.662733	14.44	13.45	13.30
DFT/D95**	$C_{2v}$	2		-225.234852	1.46	0.10	0.00
	$C_2$	0		-225.237182	0.00	0.00	0.15
	$C_s$	0		-225.235506	1.05	0.43	0.91
	$C_1$	1		-225.235484	1.07	0.27	0.33
	$C_s'$	1		-225.224584	7.91	7.33	7.31
	$C_s''$	1		-225.214070	14.50	13.20	13.45



**Figure 4.1.** Energetic relationships between stationary points on potential surface for urea monomer. B3PW91/D95\*\* relative energies before vibrational corrections are presented with MP2/D95\*\* values in parentheses.

**Table 4.2.** Results of semiempirical and ab initio calculations for urea conformers. Total energy, au (or, in case of semiempirical methods, the heat of formation, kcal/mol) for planar conformation is given for each method. NI - number of imaginary frequencies (0 characterizes energy minimum, 1 - saddle point, op – no frequency calculations, optimization only);  $\Delta E$  - relative energy of conformers, kcal/mol;  $\Delta\Delta H_0$  - relative energy with zero point vibration correction, kcal/mol;  $\Delta\Delta H_{298}$  - relative energy corrected for thermal vibrations at 298K, kcal/mol;  $m_D$  - dipole moment, D.

Basis set, Symmetry	IF	$\Delta\mu$	$\Delta E$	$\Delta\Delta H_0$	$\Delta\Delta H_{298}$	IF	$\Delta\mu$	$\Delta E$	$\Delta\Delta H_0$	$\Delta\Delta H_{298}$	IF	$\Delta\mu$	$\Delta E$	$\Delta\Delta H_0$	$\Delta\Delta H_{298}$
Semiempirical				AM1, -44.08					SAM1, -44.07					PM3, -40.96	
C <sub>2v</sub>	1	4.13			0.87	1	4.23			0.04	2	4.07			6.05
C <sub>2</sub>	0	3.59			0.00	0	4.13			0.00	0	3.02			0.00
C <sub>s</sub>											0	3.82			1.19
6-31G*				HF, -223.982192					MP2(full), -224.617929						
C <sub>2v</sub>	2	4.60	1.57	0.08	0.00	2	4.74	2.59	1.06	0.86	0				
C <sub>2</sub>	0	3.85	0.00	0.00	0.17	0	3.78	0.00	0.00	0.00	0				
C <sub>s</sub>	1	4.60	1.31	0.32	0.44	0	4.73	1.70	1.12	1.38	0				
D95**				HF, -224.046152					MP2(full), -224.681770					B3PW91, -225.234852	
C <sub>2v</sub>	2	4.70	1.29	0.00	0.00	2	4.85	2.49	1.04	0.84	2	4.43	1.46	0.10	0.00
C <sub>2</sub>	0	4.01	0.00	0.14	0.37	0	3.92	0.00	0.00	0.00	0	3.74	0.00	0.00	0.15
C <sub>s</sub>	0	4.69	1.04	0.35	1.05	0	4.82	1.44	1.01	1.20	0	4.43	1.05	0.43	0.91
D95++**				HF, -224.050373					MP2, -224.694839					B3PW91, -225.242745	
C <sub>2v</sub>	2	4.73	1.32	0.00	0.00	2	4.89	3.08	1.35	1.23	2	4.51	1.32	0.00	0.00
C <sub>2</sub>	0	4.05	0.00	0.14	0.40	0	3.96	0.00	0.00	0.00	0	3.84	0.00	0.05	0.30
C <sub>s</sub>	0	4.68	0.96	0.48	1.03	0	4.79	1.16	0.91	1.03	0	4.46	0.87	0.41	0.93
6-311++G**				HF, -224.060855					MP2, -224.752121					B3PW91, -225.258980	
C <sub>2v</sub>	2	4.69	0.73	0.00	0.00	2	4.82	2.75	1.05	0.92	2	4.47	0.69	0.00	0.00
C <sub>2</sub>	0	4.06	0.00	0.19	0.38	0	3.95	0.00	0.00	0.00	0	3.87	0.00	0.18	0.38
C <sub>s</sub>	1	4.65	0.61	0.18	0.34	0	4.73	1.20	0.89	1.03	0	4.43	0.55	0.22	0.72
6-311+G(3df,2p)				HF, -224.080708					MP2, -224.887657					B3PW91, -225.274381	
C <sub>2v</sub>	2	4.59	0.58	0.00	0.00	op	4.72	1.19	0.00	0.00	2	4.38	0.59	0.00	0.00
C <sub>2</sub>	0	4.06	0.00	0.26	0.47	op	3.91	0.00	0.51	0.64	0	3.86	0.00	0.21	0.43
C <sub>s</sub>	1	4.56	0.49	0.17	0.35	op	4.68	0.86	1.06	1.33	1	4.35	0.47	0.15	0.31

depicts the various possible structures for the urea monomer and transition states between them. The energetic data of Table 4.2 show that none of the methods used found a planar minimum for the monomeric urea molecule. Most *ab initio* methods (before vibrational correction) and PM3 found two negative vibrational frequencies for planar urea, while HF/6-31G\*, AM1 and SAM1 each found only one.

*Ab initio* methods using medium basis sets, all MP2 and PM3 calculations predict two minima on the potential energy surface: (a) an anti-conformation of C<sub>2</sub>

symmetry with the H's of the NH<sub>2</sub> groups located on opposite sides of the molecule, and (b) a less stable syn-conformation C<sub>s</sub>, with the H's of the NH<sub>2</sub> groups located on the same side. The conversion between these two conformations could occur either by inversion (via transition-state C<sub>1</sub>) or rotation (via transition states C<sub>s</sub>', C<sub>1</sub>''). The HF method at TZ basis sets predicts syn-conformation to be a transition state, and the DFT result depends on the number of polarization functions used.

In order to properly compare the energies obtained from *ab initio* calculations (which give  $\Delta E$ 's) with those obtained from semiempirical calculations (which give  $\Delta H$ 's) thermal and vibrational corrections must be applied to the *ab initio* results. After application of zero-point vibrational correction all *ab initio* methods predict the planar, C<sub>2v</sub>, to be only slightly less stable than the C<sub>2</sub> at smaller basis sets. As the size of the basis set increases, C<sub>2</sub> becomes more stable (by 0 to 0.4 kcal/mol). The inversion in stability is observed at D95\*\* for HF, D95++\*\* for DFT, and 6-311+G(3df,2p) for MP2. AM1 predicts the C<sub>2</sub> structure to be more stable than the C<sub>2v</sub> by 0.9 kcal/mole, in agreement with the MP2 calculations in the medium basis sets. SAM1 favors the C<sub>2v</sub> by less than 0.1 kcal/mol. PM3, on the other hand favors the C<sub>2</sub> structure by over 6 kcal/mol in clear disagreement with all the others. The largest energy range among the three structures among the *ab initio* results is 1.45 kcal/mol for MP2(full)/6-31G\*.

While the best calculations predict planar urea in the gas phase, one should note that the calculated dipole moments of the C<sub>2</sub> structure are consistently in better agreement with the reported gas phase experimental value of 3.83 D<sup>92</sup> and the calculated dipole moments of the planar C<sub>2v</sub> structure are in better agreement with solution experimental value of 4.2 D.<sup>91</sup> However, HF calculations generally overestimate dipole moments. MP2 calculations, while usually significantly better

than HF, still often overestimate dipoles.<sup>1</sup>

The internal rotations of the urea molecule were the subjects of previous theoretical studies. Rotational barriers of about 8-9 kcal/mol have been reported for the lower barrier<sup>2</sup> and 13.5-14.3 kcal/mol for the higher.<sup>2c</sup> We have calculated similar values of 8.5 and 13.7 (HF/D95\*\*), 6.8 and 12.8 (MP2/D95\*\*), and 7.3 and 13.4 kcal/mol (DFT/D95\*\*) after thermal correction (Table 4.1, Figure 4.1).

The apparent planarity of the molecule after vibrational correction argues that the barrier for inversion should be zero or very close to zero. A TS with one pyramidal and one planar NH<sub>2</sub> group was studied for the first time. Its uncorrected energy is intermediate between C<sub>2</sub> and C<sub>2v</sub>, lying below C<sub>s</sub> after ZPVE and thermal correction for all *ab initio* methods. The C<sub>2v</sub> structure becomes the most stable after vibrational corrections at the MP2/6-311G+(3df,2p) level. Therefore, one can effectively consider the urea molecule as planar. These results agree with the recent microwave spectroscopic investigation of the urea molecule in the gas phase.<sup>3</sup> The experiment shows the zero-point vibration to be above the planarization barrier. The nuclear wavefunction is symmetric, with the planar conformation as the average.

Selected geometrical information of the monomers is collected in Table 4.3. The semiempirical calculations tend to have longer C-N and shorter C=O distances than the best (MP2 and DFT) calculations, while the HF calculations tend to have shorter C-N and longer C=O distances. We compared calculated rotational constants to the experimental values from MW study.<sup>3</sup> The results of comparison are presented on the Table 4.4. The best agreement is found for MP2/6-311++G\*\*, and DFT/D95\*\* values for planar structure and DFT/6-311++G\*\* values for nonplanar conformation. MP2 with smaller basis set and HF calculations do not agree well with experimental values.

**Table 4.3.** Optimized geometrical parameters for urea conformers

method	sym	R(CO)	r(CN)	r(CN')	r(NH <sub>a</sub> )	OCNH <sub>a</sub>	r(N'H <sub>a</sub> )	OCN'H <sub>a</sub>	r(NH <sub>s</sub> )	OCNH <sub>s</sub>	r(N'H <sub>s</sub> )	OCN'H <sub>s</sub>
AM1	C <sub>2v</sub>	1.258	1.390		0.984	180.0			0.988	0.0		
	C <sub>2</sub>	1.256	1.403		0.991	155.6			0.994	14.1		
	C <sub>s</sub> '	1.254	1.449	1.376	0.987	180.0	1.002	59.7	0.989	0.0	1.002	300.3
	C <sub>s</sub> "	1.199	1.433	1.349	0.992	180.0	1.004	126.6	0.994	0.0	1.004	233.4
SAM1	C <sub>2v</sub>	1.279	1.391		0.988	180.0			0.989	0.0		
	C <sub>2</sub>	1.278	1.393		0.989	169.3			0.099	6.6		
	C <sub>s</sub> '	1.264	1.431	1.392	0.989	180.0	1.002	61.0	0.990	0.0	1.002	299.0
	C <sub>s</sub> "	1.264	1.431	1.392	0.989	180.0	0.997	113.7	0.990	0.0	0.997	246.3
PM3	C <sub>2v</sub>	1.233	1.405		0.990	180.0			0.990	0.0		
	C <sub>2</sub>	1.227	1.430		0.996	146.5			0.997	17.6		
	C <sub>s</sub>	1.228	1.428		0.995	147.3			0.996	16.7		
	C <sub>1</sub>	1.230	1.438	1.399	0.990	182.2	0.996	139.7	0.997	12.6	0.991	358.4
	C <sub>s</sub> '	1.229	1.468	1.387	0.990	180.0	0.999	59.7	0.990	0.0	0.999	300.3
	C <sub>s</sub> "	1.219	1.465	1.406	0.990	180.0	0.997	119.0	0.991	0.0	0.997	241.0
	C <sub>1</sub> '	1.225	1.468	1.409	0.994	159.0	0.999	53.8	0.994	22.7	0.999	294.1
	C <sub>1</sub> "	1.216	1.464	1.434	0.996	145.6	0.998	123.5	0.997	14.8	0.998	245.2
	C <sub>2v</sub>	1.205	1.364		0.991	180.0			0.992	0.0		
	C <sub>2</sub>	1.201	1.376		0.995	151.0			0.996	12.6		
	C <sub>s</sub>	1.203	1.370		0.993	163.6			0.994	12.8		
	C <sub>1</sub>	1.203	1.372	1.368	0.993	160.9	0.992	192.9	0.994	13.4	0.994	348.5
HF/D95**	C <sub>s</sub> '	1.199	1.433	1.349	0.992	180.0	1.004	56.6	0.994	0.0	1.004	303.4
	C <sub>s</sub> "	1.192	1.365	1.429	0.991	180.0	1.001	119.6	0.994	0.0	1.001	240.4
	C <sub>1</sub> "	1.192	1.367	1.429	0.992	170.6	1.001	118.6	0.995	7.0	1.001	239.6
	C <sub>2v</sub>	1.204	1.364		0.992	180.0			0.993	0.0		
HF/D95++**	C <sub>2</sub>	1.201	1.376		0.996	151.6			0.996	12.8		
	C <sub>s</sub>	1.203	1.370		0.994	162.8			0.995	13.8		
	C <sub>2v</sub>	1.232	1.381		1.005	180.0			1.006	0.0		
MP2/D95**	C <sub>2</sub>	1.229	1.397		1.011	146.5			1.011	14.7		
	C <sub>s</sub>	1.230	1.392		1.009	157.4			1.009	18.3		
	C <sub>1</sub>	1.231	1.399	1.380	1.010	149.7	1.006	184.8	1.011	17.0	1.006	349.8
	C <sub>s</sub> '	1.221	1.360	1.452	1.007	180.0	1.020	55.5	1.008	0.0	1.020	304.5
	C <sub>s</sub> "	1.223	1.380	1.449	1.005	180.0	1.017	121.7	1.008	0.0	1.017	238.3
	C <sub>1</sub> "	1.222	1.387	1.449	1.007	163.0	1.017	119.5	1.010	13.0	1.017	236.0
	C <sub>2v</sub>	1.233	1.381		1.006	180.0			1.006	0.0		
	C <sub>2</sub>	1.229	1.396		1.012	146.7			1.012	14.4		
MP2/D95++**	C <sub>s</sub>	1.231	1.393		1.010	157.2			1.011	19.5		
	C <sub>2v</sub>	1.215	1.393		1.009	145.9			1.009	14.6		
	C <sub>2</sub>	1.218	1.391		1.010	147.4			1.010	13.8		
MP2/6-311++G**	C <sub>s</sub>	1.219	1.388		1.008	157.7			1.009	18.3		
	C <sub>2v</sub>	1.228	1.374		1.007	180.0			1.007	0.0		
	C <sub>2</sub>	1.225	1.390		1.013	145.8			1.013	13.4		
MP2(full)/6-31G*	C <sub>s</sub>	1.227	1.384		1.011	157.9			1.011	16.9		

**Table 4.3.** (continued)

B3PW91/D95**	$C_{2v}$	1.226	1.378		1.006	180.0			1.007	0.0		
	$C_2$	1.223	1.390		1.011	149.1			1.011	13.2		
	$C_s$	1.225	1.385		1.009	161.2			1.009	15.1		
	$C_1$	1.225	1.389	1.379	1.010	155.6	1.007	189.2	1.010	15.2	1.008	348.6
	$C_s'$	1.221	1.360	1.452	1.007	180.0	1.020	55.5	1.008	0.0	1.020	304.7
	$C_s''$	1.215	1.376	1.445	1.007	180.0	1.017	120.6	1.010	0.0	1.017	239.4
B3PW91/D95++**	$C_{2v}$	1.226	1.377		1.007	180.0			1.007	0.0		
	$C_2$	1.223	1.388		1.011	150.5			1.011	13.0		
	$C_s$	1.225	1.384		1.009	161.5			1.010	15.1		
Neutron diffraction		1.258	1.344		1.022	180.0			1.004	0.0		

**Table 4.4.** Comparison between experimental MW and calculated rotational constants (MHz).

	(NH <sub>2</sub> ) <sub>2</sub> CO			( <sup>15</sup> NH <sub>2</sub> ) <sub>2</sub> CO			Rms
Exp	11233	10369	5417	11027	9828	5220	
MP2/6-311++G**, $C_{2v}$	11175	10401	5387	10973	9859	5193	
exp-MP2, $C_{2v}$	-58	32	-30	-54	31	-27	73
MP2/6-311++G**, $C_2$	11053	10375	5409	10846	9833	5211	
exp-MP2, $C_2$	-180	6	-8	-181	5	-9	180
B3PW91/6-311++G**, $C_{2v}$	11371	10437	5442				
exp-B3PW91/6-311++G**, $C_2$	52	44	38				78
B3PW91/6-311++G**, $C_2$	11285	10413	5455				
exp-B3PW91/6-311++G**, $C_{2v}$	138	68	25				156
HF/6-311++G**, $C_{2v}$	11693	10597	5559				
exp-HF/6-311++G**, $C_2$	460	228	142				533
HF/6-311++G**, $C_{2v}$	11615	10558	5568				
exp-HF/6-311++G**, $C_2$	382	189	151				452
MP2/D95**, $C_{2v}$	11036	10347	5340				
exp-MP2/D95**, $C_{2v}$	-197	-22	-77				213
MP2/D95**, $C_2$	10897	10320	5360				
exp-MP2/D95**, $C_2$	-336	-49	-57				344
B3PW91/D95**, $C_{2v}$	11167	10331	5366				
exp-B3PW91/D95**, $C_{2v}$	-66	-38	-51				92
B3PW91/D95**, $C_2$	11057	10320	5388				
exp-B3PW91/D95**, $C_2$	-176	-49	-29				185
HF/D95**, $C_{2v}$	11527	10524	5501				
exp-HF/D95**, $C_{2v}$	294	155	84				343
HF/D95**, $C_2$	11438	10484	5516				
exp-HF/D95**, $C_2$	205	115	99				255



**Table 4.5.** Vibrational frequencies ( $\text{cm}^{-1}$ ), IR intensities (relative units), and isotope shifts ( $\text{cm}^{-1}$ ) upon deuteration for urea molecule: comparison gas phase and matrix isolation experimental data with calculated at MP2/6-311++G\*\* (MP2), B3PW91/6-311++G\*\* (DFT1), B3PW91/D95\*\* (DFT2), and HF/D95\*\* (HF) level.

	Description		frequency			frequency			intensity			Isotope shift		
			gas	MP2		DFT <sub>1</sub>	DFT <sub>2</sub>	HF	gas	MP2		matr	MP2	
				C <sub>2v</sub>	C <sub>2</sub>	C <sub>2</sub>	C <sub>2</sub>	C <sub>2</sub>		C <sub>2v</sub>	C <sub>2</sub>		C <sub>2v</sub>	C <sub>2</sub>
τ <sub>s</sub> (NH <sub>2</sub> )	syn out-of-plane H atoms	A2	-	-626	386	368	372	398	-	0	113		-141	109
ω <sub>a</sub> (NH <sub>2</sub> )	anti out-of-plane H atoms	B1	-	-552	466	433	446	475	-	507	36		-123	119
τ <sub>a</sub> (NH <sub>2</sub> )	anti rotations of NH2 groups	A1	-	290	480	473	470	512	-	0	29		82	72
δ(CN)	in-plane NCN angle bent	A1	-	482	568	524	543	584	-	2	3		90	44
ω <sub>s</sub> (NH <sub>2</sub> )	syn rotations of NH2 groups	B1	-	542	602	532	576	619	-	13	68		138	103
δ(CO)	in-plane O atom moves	B2	572	563	658	578	587	624	vw	12	291	61	57	144
ω(CO)	out-of-plane C atom moves	B1	775	735	793	782	780	683	w	0	111		20	35
ν <sub>s</sub> (CN)	in-plane C-N bonds stretch, symm	A1	1023	977	960	961	961	1029	m	16	11	115	116	98
ρ <sub>a</sub> (NH <sub>2</sub> )	in-pane HNC angles bent, asymm	B2	1157	992	1066	1038	1048	1151	m	15	30		190	201
ρ <sub>s</sub> (NH <sub>2</sub> )	in-pane HNC angles bent, symm	A1	1157	1149	1198	1172	1176	1278	m	0.1	4		163	202
ν <sub>a</sub> (CN)	in-plane C-N bonds stretch, asymm	B2	1394	1427	1419	1415	1427	1538	s	260	220	-14	-38	-9
δ <sub>s</sub> (NH <sub>2</sub> )	in-plane HNH angles bent, symm	A1	1604	1638	1637	1624	1627	1776	s	285	187	371	373	389
δ <sub>a</sub> (NH <sub>2</sub> )	in-plane HNH angles bent, asymm	B2	1749	1636	1647	1625	1632	1785	s	0.1	0.4		484	475
ν(CO)	C=O bond stretch	A1	1776	1807	1820	1804	1835	1978	s	566	445	11	17	20
ν <sub>s</sub> (NH <sub>2</sub> )	inphase N-H bonds stretch, asymm	B2	3434	3805	3729	3596	3616	3831	vs	45	31	900	985	972
ν <sub>s</sub> (NH <sub>2</sub> )	inphase N-H bonds stretch, symm	A1	3460	3808	3729	3601	3620	3835	vs	80	49	900	984	971
ν <sub>a</sub> (NH <sub>2</sub> )	antiphase N-H bonds stretch, asymm	B2	3533	3662	3607	3715	3744	3960	vs	88	56	935	1019	1001
ν <sub>a</sub> (NH <sub>2</sub> )	antiphase N-H bonds stretch, symm	A1	3559	3670	3611	3716	3744	3960	vs	11	5	935	1018	1000

## 4.2 Vibrational frequencies calculations for the urea molecule

The vibrational frequency calculations were performed on  $C_2$  and  $C_{2v}$  conformations of the monomer. Although it is common practice to apply a scaling factor of 0.85-0.97 depending on the level of theory used<sup>4</sup> to *ab initio* frequencies in order to better reproduce experimental values, we avoid such scaling. The non-scaled results for the highest level MP2/6-311++G\*\* are presented in Table 4.5 together with experimental gas-phase spectra. The frequencies at DFT and HF level are also shown for comparison. One can see that HF significantly overestimates frequencies, while DFT gives values closer to the experimental ones than MP2 does. Basis set effects are relatively small. The  $R^2$  deviation from experimental values is insignificantly better for the  $C_{2v}$  (0.990), than for the  $C_2$  (0.989) conformer. We also calculated vibrational frequencies for the deuterated urea. Unfortunately, experimental gas-phase data are incomplete (only C=O and N-H stretching frequencies were reported), and we compare calculated isotope shifts with experimental matrix-isolation data (Table 4.4). This time preference toward planar conformation is more pronounced ( $R^2$  is 0.999 for  $C_{2v}$  and 0.996 for  $C_2$ ). We can therefore conclude that comparison of calculated and experimental IR spectra present weak evidence in favor of planar conformation of urea in the gas phase.

## 4.3 Planarization barrier in the thiourea molecule

Conformational behavior of the thiourea molecule is very similar to that of urea. The results for the thiourea monomer are summarized in Table 4.6. At the HF/D95\*\* level, the planar conformation is the only critical point on the surface.

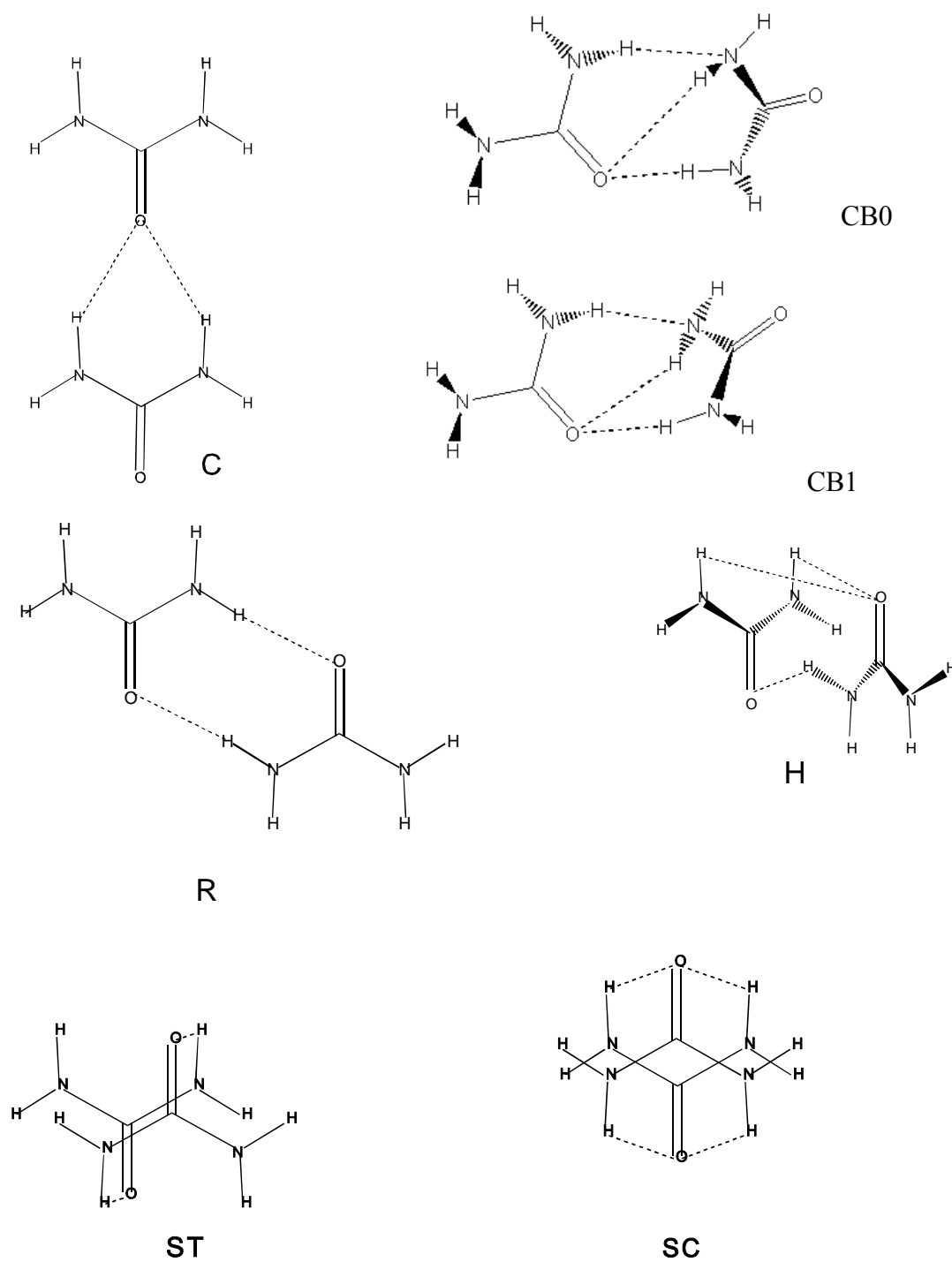
**Table 4.6.** Energetic results of ab initio calculation on thiourea monomer. Total energies in hartree, others in kcal/mol.

Method	Symmetry	Total Energy, au	$\Delta E$ , kcal/mol	$\Delta H_0$ , kcal/mol	$\Delta H_{298}$ , kcal/mol
HF/D95**	$C_{2v}$	-546.652508	0.00	0.00	0.00
DFT/D95**	$C_{2v}$	-548.143869	0.73	0.00	0.00
DFT/D95**	$C_2$	-548.145032	0.00	0.49	0.82
DFT/D95**	$C_s$	-548.143977	0.66	0.30	0.58
MP2/D95**	$C_{2v}$	-547.238024	1.50	0.15	0.00
MP2/D95**	$C_2$	-547.240409	0.00	0.00	0.10
MP2/D95**	$C_s$	-547.238691	1.08	0.52	0.91

Using DFT and/or MP2 with the same basis set resulted in minima representing anti- and syn- conformers, as in the case of urea. However, the planar barrier for thiourea is about half that of urea. Like urea, the thiourea becomes planar after zero-point corrections are applied.

#### 4.4 Conformations of the dimers

The results of the calculations on the dimers are collected in Tables 4.7-4.9. The geometric analysis for the dimers becomes somewhat complex due to: (a) the possible combinations of monomer conformations that can statistically occur in the dimer, (b) the different possibilities of intermolecular interactions. We located four general classes of dimeric interactions: chain dimers, **C**, ribbon dimers, **R**, herringbone dimers, **H**, and stacked dimers, **S** (Figure 4.2). The first three of these structure types



**Figure 4.2.** Conformations and notations for urea dimers

(**C**, **R**, and **H**) correspond to minima on the potential surface, while stacked dimers correspond to saddle points between **C** and **R** dimers. All four of these kinds of interactions play important roles in the crystal structures of urea and thiourea. The **C** interactions are similar to those in the linear chains found in urea crystals while the T-shaped interactions **H** are representative of the inter-chain interactions in these crystals. The **R** interactions form the ‘ribbon’-like structure of the thiourea crystals, while the **C** interactions link the ribbons together. **S** interactions are typical for many crystals with planar molecules and were found<sup>5</sup> to be the most stable configuration for the dimers of acetone molecules with molecular shape similar to urea. The fragments of urea and thiourea crystal structures are shown in Figure 3.4-3.5.

In order to better compare the MO optimized geometries with experimental crystal structures, we imposed geometrical constraints in some calculations. For the chains, we optimized the geometries with (a) both molecules constrained to be planar and geometrically equivalent, **CE**; (b) planar but geometrically different (flat chain), **CF**; (c) collinear C=O bonds, but not planar (linear chain), **CL**; and (d) no constraints (bent chain), **CB**. The **CE** structure mimics the translational symmetry of the urea crystal. In the **CB** structure, one urea molecule is turned to form an additional H-bond between the H<sub>s</sub> atom of one monomer and one of N atoms of the other. For the ribbons, we (a) enforced both a twofold axis and a plane of symmetry for each molecule (equivalent ribbon), **RE**; (b) enforced only a plane of symmetry (flat ribbon), **RF**; (c) no constraints, centrosymmetric dimer with heavy atoms in parallel planes (parallel ribbon), **RP**; and (d) no constraints, C<sub>2</sub> dimer (twisted ribbon), **RT**. The **RE** mimics idealized crystal structure with planar ribbons, **RP** mimics mutual orientation of the molecules found in high-temperature phase, and **RT** in low-temperature phase, reported for the orthogonal thiourea. Inclusion compounds also contain dimers of **RT**

**Table 4.7.** *Ab initio* and semiempirical results for urea dimers: I.F. - number of imaginary frequencies; approximate symmetry marked \*;  $\Delta\Delta H_{298}$  (interaction enthalpy, kcal/mol) is defined as the difference between  $\Delta H_{298}$  for the dimer and monomers in  $C_2$  conformation. Interaction energy with the reference to the planar (non-equilibrium) monomers shown in brackets. X...Y denotes symmetrically-independent intermolecular distances (Å) between the atom X of the first monomer and the atom Y of the second monomer.

	type	Sym	IF	Monomer sym.	$\Delta\Delta H_{298}$	H...O	H...O	O...H	N...H	N...H	C...O	O...C
MP2/D95++**	CF	$C_{2v}$	op	$C_{2v}$	$C_{2v}$	-3.78(-4.57)	2.116	2.116				
MP2/D95**	CF	$C_{2v}$	op	$C_{2v}$	$C_{2v}$	-4.73(-5.05)	2.104	2.104				
DFT/D95**	CF	$C_{2v}$	5	$C_{2v}$	$C_{2v}$	-6.17(-5.87)	2.122	2.122				
HF/D95++**	CF	$C_{2v}$	5	$C_{2v}$	$C_{2v}$	-7.23(-6.43)	2.242	2.242				
HF/D95**	CF	$C_{2v}$	5	$C_{2v}$	$C_{2v}$	-7.26(-6.52)	2.222	2.222				
AM1	CF	$C_{2v}$	4	$C_{2v}$	$C_{2v}$	-4.41(-6.15)	2.209	2.209				
PM3	CF	$C_{2v}$	4	$C_{2v}$	$C_{2v}$	8.99(-3.11)	2.596	2.596				
PM3	CF1	$C_{2v}$	4	$C_{2v}$	$C_{2v}$	10.59(-1.49)	1.929	1.929				
SAM1	CF	$C_{2v}$	2	$C_{2v}$	$C_{2v}$	-3.92(-4.00)	1.989	1.989				
MP2/D95++**	CL	$C_2$	op	$C_2$	$C_2$	-6.12	2.163	2.163				6.12
MP2/D95**	CL	$C_2$	op	$C_2$	$C_2$	-5.41	2.145	2.145				5.41
DFT/D95**	CL	$C_2$	1	$C_2$	$C_2$	-4.03	2.155	2.155				4.03
HF/D95++**	CL	$C_2$	1	$C_2$	$C_2$	-5.50	2.272	2.272				5.50
HF/D95**	CL	$C_2$	1	$C_2$	$C_2$	-5.30	2.275	2.275				5.30
AM1	CL	$C_2$	1	$C_2$	$C_2$	-5.62	2.221	2.221				5.62
PM3	CL	$C_2$	1	$C_2$	$C_2$	-1.83	2.682	2.682				1.83
SAM1	CL	$C_2$	1	$C_{2v}$	$C_{2v}^*$	-4.05	1.991	1.991				4.05
MP2/D95++**	CB1	$C_1$	0	$C_2^*$	$C_2^*$	-6.75	1.971	2.773	2.103			6.75
MP2/D95**	CB1	$C_1$	0	$C_2^*$	$C_2^*$	-6.73	1.962	2.712	2.084			6.73
DFT/D95**	CB0	$C_1$	0	$C_2^*$	$C_2^*$	-7.05	1.908	2.933	2.070			7.05
DFT/D95**	CB1	$C_1$	0	$C_2^*$	$C_2^*$	-6.94	1.911	2.863	2.070			6.94
HF/D95++**	CB1	$C_1$	0	$C_2^*$	$C_2^*$	-5.80	2.158	2.591	2.436			5.80
HF/D95**	CB0	$C_1$	0	$C_2^*$	$C_2^*$	-5.98	2.120	2.656	2.391			5.98
HF/D95**	CB1	$C_1$	0	$C_2^*$	$C_2^*$	-6.17	2.131	2.613	2.411			6.17
AM1	CB0	$C_1$	0	$C_2^*$	$C_2^*$	-6.55	2.205	2.239	2.645			6.55
AM1	CB1	$C_1$	0	$C_2^*$	$C_2^*$	-6.57	2.177	2.260	2.617			6.57
AM1	CB2	$C_1$	0	$C_s^*$	$C_2^*$	-6.68	2.176	2.182	2.724	2.752		6.68
SAM1	CB2	$C_s^*$	0	$C_s^*$	$C_{2v}^*$	-4.19	1.995	1.995	3.844	3.856		4.19
SAM1	CB3	$C_1$	0	$C_{2v}^*$	$C_{2v}^*$	-4.42	1.871	3.103	3.448	3.878		4.42
PM3	CB0	$C_1$	0	$C_2^*$	$C_2^*$	-2.59	1.840	3.707	2.696			2.59
PM3	CB1	$C_1$	0	$C_2^*$	$C_2^*$	-2.52	1.838	3.544	2.833			2.52
PM3	CB2	$C_1$	0	$C_2^*$	$C_s^*$	-1.62	1.840	1.840	2.692			1.62

**Table 4.7.** *Ab initio* and semiempirical results for urea dimers (continued)

PM3	CB3	C <sub>1</sub>	0	C <sub>s</sub> *	C <sub>2</sub> *	-2.26	1.835	3.007	3.269	3.878	2.26
PM3	CB4	C <sub>1</sub>	0	C <sub>s</sub> *	C <sub>s</sub> *	-1.31	1.832	3.027	3.244	3.746	1.31
PM3	CB5	C <sub>1</sub>	0	C <sub>s</sub> *	C <sub>s</sub> *	-1.29	1.835	2.898	3.201	4.632	1.29
PM3	CB6	C <sub>1</sub>	0	C <sub>2</sub> *	C <sub>2</sub> *	-2.29	1.835	3.608	3.326	4.594	2.29
PM3	CB7	C <sub>1</sub>	0	C <sub>2</sub> *	C <sub>2</sub> *	-2.25	1.835	3.512	3.275	5.154	2.25
PM3	CB8	C <sub>1</sub>	0	C <sub>s</sub> *	C <sub>2</sub> *	-2.34	1.836	2.915	3.275	5.154	2.34
PM3	CB9	C <sub>1</sub>	1	C <sub>e</sub> *	C <sub>e</sub> *	-1.16	2.715	2.699	4.539	5.240	1.16
MP2/D95++**	RF	C <sub>2h</sub>	op	C <sub>2v</sub> *	C <sub>2v</sub> *	-6.18(-8.88)					
MP2/D95**	RF	C <sub>2h</sub>	op	C <sub>2v</sub> *	C <sub>2v</sub> *	-7.38(-9.47)					
DFT/D95**	RF	C <sub>2h</sub>	5	C <sub>2v</sub> *	C <sub>2v</sub> *	-11.82(-11.52)					
HF/D95++**	RF	C <sub>2h</sub>	5	C <sub>2v</sub> *	C <sub>2v</sub> *	-10.07(-9.27)					
HF/D95**	RF	C <sub>2h</sub>	5	C <sub>2v</sub> *	C <sub>2v</sub> *	-10.13(-8.03)					
AM1	RF	C <sub>2h</sub>	3	C <sub>2v</sub> *	C <sub>2v</sub> *	-6.90(-8.64)	2.036	2.036			
PM3	RF	C <sub>2h</sub>	4	C <sub>2v</sub> *	C <sub>2v</sub> *	4.07(-8.03)	1.792	1.792			
PM3	RF	C <sub>2h</sub>	4	C <sub>2v</sub> *	C <sub>2v</sub> *	7.99(-4.09)	2.410	2.410			
SAM1	RF	C <sub>2h</sub>	0	C <sub>2v</sub> *	C <sub>2v</sub> *	-8.34(-8.42)	1.801	1.801			
MP2/D95++**	RP	C <sub>i</sub>	0	C <sub>2</sub> *	C <sub>2</sub> *	-8.56	1.874	1.874			8.56
MP2/D95**	RP	C <sub>i</sub>	0	C <sub>2</sub> *	C <sub>2</sub> *	-8.46	1.870	1.870			8.46
DFT/D95**	RP	C <sub>i</sub>	0	C <sub>2</sub> *	C <sub>2</sub> *	-10.22	1.803	1.803			10.22
HF/D95++**	RP	C <sub>i</sub>	0	C <sub>2</sub> *	C <sub>2</sub> *	-8.30	2.006	2.006			8.30
HF/D95**	RP	C <sub>i</sub>	0	C <sub>2</sub> *	C <sub>2</sub> *	-8.41	1.992	1.992			8.41
AM1	RP	C <sub>i</sub>	0	C <sub>2</sub> *	C <sub>2</sub> *	-8.56	2.071	2.071			8.56
PM3	RP	C <sub>i</sub>	0	C <sub>2</sub> *	C <sub>2</sub> *	-5.75	1.813	1.813			5.75
PM3	RP2	C <sub>i</sub>	0	C <sub>2</sub> *	C <sub>2</sub> *	-4.15	1.811	1.811			4.15
PM3	RP3	C <sub>1</sub>	0	C <sub>2</sub> *	C <sub>2</sub> *	-4.91	1.811	1.813			4.91
MP2/D95++**	RT	C <sub>2</sub>	0	C <sub>2</sub> *	C <sub>2</sub> *	-8.55	1.874	1.874			8.55
MP2/D95**	RT	C <sub>2</sub>	0	C <sub>2</sub> *	C <sub>2</sub> *	-8.47	1.870	1.870			8.47
DF/D95**	RT	C <sub>2</sub>	0	C <sub>2</sub> *	C <sub>2</sub> *	-10.24	1.804	1.804			10.24
HF/D95++**	RT	C <sub>2</sub>	0	C <sub>2</sub> *	C <sub>2</sub> *	-8.31	1.993	1.993			8.31
HF/D95**	RT	C <sub>2</sub>	0	C <sub>2</sub> *	C <sub>2</sub> *	-8.41	1.993	1.993			8.41
AM1	RT	C <sub>2</sub>	0	C <sub>2</sub> *	C <sub>2</sub> *	-8.86	2.088	2.088			8.86
PM3	RT	C <sub>2</sub>	0	C <sub>2</sub> *	C <sub>2</sub> *	-4.66	1.847	1.847			4.66
PM3	RT2	C <sub>2</sub>	0	C <sub>s</sub> *	C <sub>s</sub> *	-3.93	1.814	1.814			3.93
PM3	RT3	C <sub>2</sub>	0	C <sub>s</sub> *	C <sub>s</sub> *	-2.44	2.603	2.603			2.44 3.559
PM3	RT4	C <sub>1</sub>	0	C <sub>2</sub> *	C <sub>s</sub> *	-3.30	2.551	2.652			3.30 3.524
PM3	RT5	C <sub>2</sub>	0	C <sub>2</sub> *	C <sub>2</sub> *	-4.01	2.548	2.548			4.01 3.774
PM3	RT6	C <sub>1</sub>	0	C <sub>2</sub> *	C <sub>2</sub> *	-4.66	1.825	2.500			4.66 3.718
PM3	RT7	C <sub>1</sub>	0	C <sub>2</sub> *	C <sub>s</sub> *	-3.98	1.824	2.586			3.98 3.542
PM3	RT8	C <sub>1</sub>	0	C <sub>s</sub> *	C <sub>s</sub> *	-3.04	1.823	2.601			3.04 3.507
PM3	RT9	C <sub>1</sub>	0	C <sub>s</sub> *	C <sub>2</sub> *	-3.78	1.825	2.513			3.78 3.678

**Table 4.7.** Dimers of urea (continued)

PM3	RTA	C <sub>1</sub>	0	C <sub>s</sub> *	C <sub>s</sub> *	-2.87	1.823	2.542	2.87	3.609	
PM3	RTB	C <sub>1</sub>	0	C <sub>2</sub> *	C <sub>s</sub> *	-3.76	1.823	2.557	3.76	3.579	
PM3	RTC	C <sub>1</sub>	0	C <sub>2</sub> *	C <sub>2</sub> *	-2.37	1.825	2.518	2.37	3.718	
DFT/D95**	HB	C <sub>1</sub>	0	C <sub>s</sub> *	C <sub>2</sub> *	-3.34	2.962	3.468	1.925	3.34	
HF/D95**	HB	C <sub>1</sub>	0	C <sub>s</sub> *	C <sub>2</sub> *	-3.77	3.221	3.306	2.090	3.77	
AM1	HB	C <sub>1</sub>	0	C <sub>s</sub> *	C <sub>2</sub> *	-6.71	2.582	2.618	2.139	6.71	
SAM1	HB	C <sub>1</sub>	0	C <sub>s</sub> *	C <sub>2</sub> *	-3.67	2.932	2.946	1.858	3.67	
PM3	HB	C <sub>1</sub>	1	C <sub>s</sub> *	C <sub>2</sub> *	-3.06	3.253	3.268	2.543	3.06	
PM3	HB1	C <sub>1</sub>	1	C <sub>s</sub> *	C <sub>s</sub> *	-2.07	3.096	3.993	2.543	2.07	
PM3	HB2	C <sub>1</sub>	1	C <sub>s</sub> *	C <sub>s</sub> *	-2.24	3.162	3.752	2.550	2.24	
PM3	HB3	C <sub>1</sub>	1	C <sub>s</sub> *	C <sub>s</sub> *	-2.08	3.100	3.940	2.544	2.08	
DFT/D95**	ST0	C <sub>2h</sub>	2	C <sub>s</sub>	C <sub>s</sub>	-1.75				1.75	
DFT/D95**	ST1	C <sub>i</sub>	1	C <sub>2</sub> *	C <sub>2</sub> *	-3.32				3.32	
HF/D95**	ST0	C <sub>2h</sub>	2	C <sub>s</sub>	C <sub>s</sub>	-1.88				1.88	
HF/D95**	ST1	C <sub>i</sub>	1	C <sub>2</sub> *	C <sub>2</sub> *	-3.36				3.36	
AM1	ST0	C <sub>2h</sub>	2	C <sub>s</sub>	C <sub>s</sub>	-1.98				1.98	
SAM1	ST0	C <sub>2h</sub>	3	C <sub>s</sub>	C <sub>s</sub>	-1.60	4.014	4.014	4.014	1.60	4.245
PM3	ST0	C <sub>2h</sub>	2	C <sub>s</sub>	C <sub>s</sub>	-1.67	3.722	3.722	3.722	1.67	3.221

type. For herringbone dimers, we (a) used no constraints, **HB**; (b) enforced a plane of symmetry (flat herringbone), **HF**, and (c) constrained molecules to be geometrically equivalent, have antiparallel C=O bonds, and be planar with molecular planes perpendicular to each other (equivalent herringbone), **HE**. For the stacking dimers we imposed C<sub>2h</sub> (**ST**) or centrosymmetric (**SC**) structures. Without these constraints, the optimizations of the stacked dimers converged to the chain or ribbon dimers. The energetic data for the dimers are presented in Tables 4.7-4.8. For the PM3 calculations, the planarization energy more than canceled the stabilization due to H-bond formation, resulting in net repulsion. For this reason we list pure H-bonding stabilization (the difference between  $\Delta H_f$ 's for planar dimers and monomers) in brackets.

Only **CB**, **RP**, **RT** and **HB** are true minima on the potential surface as only



they have no imaginary vibrational frequencies. The *ab initio* and AM1 calculations (Table 4.7) agree reasonably well both for geometries and interaction enthalpies. Since the **CE**, **RE** and **HE** dimers are not stationary points on the potential surface, we approximated the zero-point vibrational and thermal corrections using the corresponding results for **CF** and **RF**. Due to computational limitations, frequency calculations were not possible at the MP2/D95++\*\* level. We used the MP2/D95\*\* calculations to estimate the vibrational corrections. Despite the fact that the planar dimers can have as many as five imaginary frequencies, all thermally corrected HF calculations predict the relaxed planar dimers (**CF** and **RF**) to be the most stable of each type (chain or ribbon). The corresponding thermally corrected MP2 structures remain pyramidal about the nitrogens. However, the enthalpies required to planarize the dimers are much less than required to planarize two monomers (except for the **CB** type structures which have an additional H-bond not possible in the crystal). Together with our earlier conclusion that the monomer is effectively planar (see above), this suggests that a growing aggregate would likewise tend to be planar, in accord with the crystal structure. The corrected DFT calculations predict planar dimers (once again except for **CB** dimers). However, the enthalpy required for planarization of the **CB** dimers is quite small (0.9 kcal/mol). All *ab initio* methods predict the uncorrected planarization energies of the **CL**, **RP**, and **RT** dimers to be similar to that of the monomer. Thus, the H-bond overcomes the planarization barrier of the second molecule. To illustrate this point, we optimized the transition state for NH<sub>2</sub> group inversion in a ribbon dimer, **RTP** (a saddle point between **RP** and **RT** conformers). The uncorrected inversion barrier is significantly lower than that of the monomer (0.7 vs. 1.0 kcal/mol in both HF/D95\*\* and DFT/D95\*\*).

Among the semiempirical methods, AM1 produces the closest agreement to

**Table 4.8.** Ab initio results for urea dimers: IF - number of imaginary frequencies; approximate symmetry marked \*;  $E_{\text{rel}}$  - relative energy, kcal/mol;  $\Delta E$  - interaction energy of molecules in dimer (relative to  $C_2$  conformation); cp - counterpoise basis set superposition error correction, kcal;  $\Delta\Delta H_0$ ,  $\Delta\Delta H_{298}$  - interaction enthalpy, kcal/mol;

Method	type	sym	IF	Monomer	$\Delta\mu$	$E_{\text{rel}}$	$\Delta E$	$\Delta E_{\text{cp}}$	$\Delta\Delta H_0$	$\Delta\Delta H_0_{\text{cp}}$	$\Delta\Delta H_{298}$	$\Delta\Delta H_{298}_{\text{cp}}$
HF/D95**	CE	$C_{2v}$	op	$C_{2v}$ $C_{2v}$	10.85	5.55	-6.06	-5.37	-7.86	-7.17	-7.83	-7.14
HF/D95**	CF	$C_{2v}$	5	$C_{2v}$ $C_{2v}$	10.89	5.41	-6.19	-5.49	-7.99	-7.29	-7.96	-7.26
HF/D95**	CL	$C_2$	1	$C_2$ $C_2$	10.11	4.27	-7.33	-6.48	-7.09	-6.24	-6.15	-5.30
HF/D95**	CB1	$C_1$	0	$C_2^*$ $C_2^*$	6.78	2.64	-8.96	-8.35	-7.82	-7.21	-6.78	-6.17
HF/D95**	CB0	$C_1$	0	$C_2^*$ $C_2^*$	6.72	2.57	-9.03	-8.17	-7.87	-7.01	-6.84	-5.98
HF/D95**	RE	$C_{2h}$	op	$C_{2v}$ $C_{2v}$	0.00	1.75	-9.85	-8.90	-10.79	-9.84	-10.85	-9.90
HF/D95**	RF	$C_{2h}$	4	$C_{2v}^*$ $C_{2v}^*$	0.00	1.44	-10.16	-9.13	-11.10	-10.07	-11.16	-10.13
HF/D95**	RP	$C_i$	0	$C_2^*$ $C_2^*$	0.00	0.01	-11.59	-10.57	-10.36	-9.34	-9.43	-8.41
HF/D95**	RT	$C_2$	0	$C_2^*$ $C_2^*$	0.17	0.00	-11.60	-10.58	-10.37	-9.35	-9.43	-8.41
HF/D95**	RTP	$C_1$	1	$C_2^*$ $C_1$	0.70	0.70	-10.90	-9.87	-10.55	-9.52	-9.67	-8.64
HF/D95**	ST	$C_{2h}$	2	$C_s^*$ $C_s^*$	0.00	9.38	-2.22	-1.44	-2.55	-1.77	-1.88	-1.10
HF/D95**	SC	$C_i$	1	$C_2^*$ $C_2^*$	0.00	6.72	-4.88	-4.20	-4.02	-3.34	-3.36	-2.68
HF/D95**	HE	$C_s$	op	$C_{2v}$ $C_{2v}$	0.65	8.52	-3.08	-2.51	-5.04	-4.46	-4.43	-3.86
HF/D95**	HF	$C_s$	2	$C_{2v}^*$ $C_s^*$	0.50	8.34	-3.26	-2.63	-5.22	-4.59	-4.61	-3.98
HF/D95**	HB	$C_1$	0	$C_2^*$ $C_2^*$	3.86	5.01	-6.59	-5.77	-5.85	-5.03	-4.59	-3.77
HF/D95++**	CE	$C_{2v}$	op	$C_{2v}$ $C_{2v}$	10.87	5.35	-5.56	-5.24	-7.48	-7.16	-7.46	-7.14
HF/D95++**	CF	$C_{2v}$	5	$C_{2v}$ $C_{2v}$	10.91	5.24	-5.68	-5.33	-7.60	-7.60	-7.58	-7.23
HF/D95++**	CL	$C_2$	1	$C_2$ $C_2$	10.10	3.88	-7.03	-6.64	-6.73	-6.34	-5.88	-5.50
HF/D95++**	CB	$C_1$	0	$C_2^*$ $C_2^*$	6.84	2.43	-8.48	-7.93	-7.32	-6.77	-6.35	-5.80
HF/D95++**	RE	$C_{2h}$	op	$C_{2v}$ $C_{2v}$	0.00	1.85	-9.06	-8.58	-10.29	-9.81	-10.28	-9.80
HF/D95++**	RF	$C_{2h}$	4	$C_{2v}^*$ $C_{2v}^*$	0.00	1.56	-9.35	-8.86	-10.58	-10.09	-10.56	-10.07
HF/D95++**	RP	$C_i$	0	$C_2^*$ $C_2^*$	0.00	0.02	-10.89	-10.37	-9.72	-9.20	-8.82	-8.30
HF/D95++**	RT	$C_2$	0	$C_2^*$ $C_2^*$	0.14	0.00	-10.91	-10.39	-9.73	-9.21	-8.83	-8.31

**Table 4.8.** Ab initio results for the dimers of urea (continued)

DFT/D95**	CE	C <sub>2v</sub>	op	C <sub>2v</sub>	C <sub>2v</sub>	10.63	8.13	-5.58	-4.31	-7.20	-5.93	-7.27	-5.99
DFT/D95**	CF	C <sub>2v</sub>	5	C <sub>2v</sub>	C <sub>2v</sub>	10.63	7.90	-5.81	-4.49	-7.43	-6.11	-7.49	-6.17
DFT/D95**	CL	C <sub>2</sub>	1	C <sub>2</sub>	C <sub>2</sub>	10.63	6.75	-6.96	-5.84	-6.55	-5.43	-5.15	-4.03
DFT/D95**	CB1	C <sub>1</sub>	0	C <sub>2</sub> *	C <sub>2</sub> *	5.77	3.24	-10.47	-9.04	-9.13	-7.70	-8.37	-6.94
DFT/D95**	CB0	C <sub>1</sub>	0	C <sub>2</sub> *	C <sub>2</sub> *	5.71	3.19	-10.52	-9.13	-9.20	-7.81	-8.44	-7.05
DFT/D95**	RE	C <sub>2h</sub>	op	C <sub>2v</sub>	C <sub>2v</sub>	0.00	2.25	-11.46	-9.91	-12.44	-10.89	-12.70	-11.15
DFT/D95**	RF	C <sub>2h</sub>	4	C <sub>2v</sub> *	C <sub>2v</sub> *	0.00	1.59	-12.12	-10.58	-13.10	-11.56	-13.36	-11.82
DFT/D95**	RP	C <sub>i</sub>	0	C <sub>2</sub> *	C <sub>2</sub> *	0.00	0.01	-13.71	-12.12	-12.54	-10.95	-11.80	-10.22
DFT/D95**	RT	C <sub>2</sub>	0	C <sub>2</sub> *	C <sub>2</sub> *	0.27	0.00	-13.71	-12.13	-12.55	-10.97	-11.82	-10.24
DFT/D95**	RTP	C <sub>2</sub>	1	C <sub>2</sub> *	C <sub>1</sub>	0.67	0.75	-12.96	-11.35	-12.60	-10.99	-11.94	-10.33
DFT/D95**	ST	C <sub>2h</sub>	2	C <sub>s</sub> *	C <sub>s</sub> *	0.00	12.18	-1.53	-0.29	-1.73	-0.49	-1.75	-0.51
DFT/D95**	SC	C <sub>i</sub>	1	C <sub>2</sub> *	C <sub>2</sub> *	0.00	8.88	-4.83	-3.75	-3.85	-2.77	-3.32	-2.24
DFT/D95**	HE	C <sub>s</sub>	op	C <sub>2v</sub>	C <sub>2v</sub>	0.92	11.00	-2.71	-1.89	-4.68	-3.86	-4.67	-3.85
DFT/D95**	HF	C <sub>s</sub>	4	C <sub>2v</sub> *	C <sub>s</sub> *	0.78	10.82	-2.89	-2.02	-4.86	-3.99	-4.85	-3.98
DFT/D95**	HB	C <sub>1</sub>	0	C <sub>2</sub> *	C <sub>2</sub> *	3.17	7.25	-6.46	-5.22	-5.85	-4.61	-4.57	-3.34
MP2/D95**	CE	C <sub>2v</sub>	op	C <sub>2v</sub>	C <sub>2v</sub>	11.35	9.14	-5.42	-2.83	-7.24	-4.65	-7.17	-4.57
MP2/D95**	CF	C <sub>2v</sub>	5	C <sub>2v</sub>	C <sub>2v</sub>	11.40	8.94	-5.62	-2.96	-7.44	-4.78	-7.37	-4.71
MP2/D95**	CL	C <sub>2</sub>	1	C <sub>2</sub>	C <sub>2</sub>	10.16	6.38	-8.19	-6.59	-7.58	-5.98	-6.87	-5.26
MP2/D95**	CB	C <sub>1</sub>	0	C <sub>2</sub> *	C <sub>2</sub> *	6.12	1.88	-12.68	-8.91	-11.25	-7.48	-10.48	-6.71
MP2/D95**	RE	C <sub>2h</sub>	op	C <sub>2v</sub>	C <sub>2v</sub>	0.00	3.69	-10.88	-7.01	-12.15	-8.28	-12.09	-8.22
MP2/D95**	RF	C <sub>2h</sub>	4	C <sub>2v</sub> *	C <sub>2v</sub> *	0.00	3.22	-11.35	-7.38	-12.61	-8.65	-12.56	-8.60
MP2/D95**	RP	C <sub>i</sub>	0	C <sub>2</sub> *	C <sub>2</sub> *	0.00	0.02	-14.55	-10.63	-13.14	-9.22	-12.38	-8.46
MP2/D95**	RT	C <sub>2</sub>	0	C <sub>2</sub> *	C <sub>2</sub> *	0.20	0.00	-14.57	-10.64	-13.15	-9.22	-12.39	-8.46
MP2/D95**	HF	C <sub>s</sub>	2	C <sub>2v</sub> *	C <sub>s</sub> *	1.36	0.00	-2.90	-0.02	-6.13	-3.25	-2.16	0.72
MP2/D95++**	CE	C <sub>2v</sub>	op	C <sub>2v</sub>	C <sub>2v</sub>	11.38	10.35	-3.74	-1.76	-5.56	-3.58	-5.29	-3.31
MP2/D95++**	CF	C <sub>2v</sub>	op	C <sub>2v</sub>	C <sub>2v</sub>	11.43	10.17	-3.91	-1.87	-5.73	-3.69	-5.46	-3.43
MP2/D95++**	CL	C <sub>2</sub>	op	C <sub>2</sub>	C <sub>2</sub>	10.11	5.95	-8.14	-5.96	-7.53	-5.36	-6.62	-4.44
MP2/D95++**	CB	C <sub>1</sub>	op	C <sub>2</sub> *	C <sub>2</sub> *	6.03	1.59	-12.49	-8.88	-11.06	-7.45	-10.10	-6.48
MP2/D95++**	RE	C <sub>2h</sub>	op	C <sub>2v</sub>	C <sub>2v</sub>	0.00	5.04	-9.04	-5.82	-10.31	-7.09	-10.06	-6.84
MP2/D95++**	RF	C <sub>2h</sub>	op	C <sub>2v</sub> *	C <sub>2v</sub> *	0.00	4.59	-9.49	-6.18	-10.76	-7.44	-10.51	-7.19
MP2/D95++**	RP	C <sub>i</sub>	op	C <sub>2</sub> *	C <sub>2</sub> *	0.00	0.00	-14.09	-10.63	-12.67	-9.22	-11.72	-8.27
MP2/D95++**	RT	C <sub>2</sub>	op	C <sub>2</sub> *	C <sub>2</sub> *	0.16	0.00	-14.08	-10.63	-12.66	-9.21	-11.71	-8.25

the *ab initio* calculations. SAM1 does reasonably well. However, it finds neither **RP** nor **RT** minima and has another inconsistency with *ab initio* results. When optimized with no symmetry constraints, **CF** dimer is distorted at SAM1 level with one part of

the forked H-bond shorter than the other one. PM3 appears to be erratic both for energies and geometries, as it was previously noted.<sup>6</sup> For example, PM3 predicts unreasonably large enthalpies for planarization of the NH<sub>2</sub> groups in both monomers and dimers. Another peculiarity of PM3 results is the abundance of dimeric conformations (Table 4.7). In part, this is the result of strong molecular nonplanarity: all the different combinations of NH<sub>2</sub> groups pyramidal conformations are present. For the comparison, at the AM1 level (where syn-conformation does not exist for an isolated molecule) optimization of some conformers leads to spontaneous inversion, and other dimers stabilize syn-conformation for one of the molecules. However, the other kind of isomer observed at PM3 level, is bond-length isomers. For example, PM3 gives 3 minima for **RF** dimer: in one both H-bonds are 1.8 Å, in another they are both 2.4 Å, and in the third one is shorter than another. This is clearly a pitfall of PM3 calculation, which was attributed<sup>7</sup> to oscillating functional form for the core-core repulsion, implemented in PM3. We see that AM1 predicts multiple minima in only one case (**CB**). Two minima (denoted **CB0** and **CB1** in Table 4.5a) differ in the relative orientation of the molecules (see Figure 4.2). HF and DFT methods also predict these minima (we did not attempt to find them using MP2). The third minimum (**CB2**) contains one syn-urea, which is unstable as an isolated molecule using this method. Only SAM1 found a similar minimum.

Geometrical information on the dimers is collected in Table 4.9. All methods predict C=O bond lengthening upon dimerization by about 0.004 Å for the H-bond donor and 0.008 Å for the H-bond acceptor in the chain dimer, and 0.014 Å for the ribbon dimer. This correlates with shortening of the H-bond. The N-H bond involved in H-bonding formation elongates by 0.005 Å (**CF**) or 0.025 Å (**RF**), other N-H bonds change insignificantly. The C-N bonds shorten (by 0.01 Å for **CF** and 0.02 Å for **RF**)

**Table 4.9.** Bond lengths and H-bonds for planar urea monomers and dimers (Å).  
For chain dimers d and a refer to the H-donor and H-acceptor, respectively

Method		C=O	C-N	C-N'	N-H	N-H''	N'-H''	N'-H'''	H...O	H''...O
AM1	Monomer	1.258	1.390		0.984	0.988				
	CF dimer, d	1.262	1.388		0.988	0.986			2.206	
	CF dimer, a	1.262	1.387		0.985	0.988				
	RF dimer	1.268	1.382	1.391	0.988	0.996	0.985	0.987		1.988
PM3	monomer	1.232	1.405		0.990	0.990				
	CF dimer, d	1.236	1.402		0.991	0.990			2.597	
	CF dimer, a	1.236	1.402		0.990	0.990				
	RF dimer	1.245	1.391	1.403	0.989	1.011	0.990	0.990		1.792
HF/6-31G*	monomer	1.202	1.360		0.990	0.991				
HF/D95**	monomer	1.205	1.364		0.991	0.992				
	CF dimer, d	1.210	1.362		0.994	0.991			2.222	
	CF dimer, a	1.213	1.357		0.992	0.993				
	RF dimer	1.217	1.349	1.363	0.991	1.004	0.991	0.992		1.966
HF/D95++**	monomer	1.204	1.364		0.992	0.993				
	CF dimer, d	1.209	1.361		0.994	0.992			2.242	
	CF dimer, a	1.213	1.357		0.992	0.993				
	RF dimer	1.217	1.349	1.363	0.992	1.004	0.992	0.993		1.980
HF/6-311G**	monomer	1.196	1.361		0.990	0.991				
MP2/6-31G*	monomer	1.228	1.374		1.007	1.007				
MP2/D95**	monomer	1.232	1.381		1.005	1.005				
	CF dimer, d	1.237	1.379		1.009	1.005			2.104	
	CF dimer, a	1.240	1.372		1.005	1.006				
	RF dimer	1.247	1.362	1.379	1.006	1.024	1.005	1.005		1.836
MP2/D95++**	monomer	1.233	1.381		1.006	1.006				
	CF dimer, d	1.237	1.378		1.010	1.006			2.121	
	CF dimer, a	1.241	1.372		1.006	1.007				
	RF dimer	1.247	1.362	1.379	1.006	1.024	1.006	1.006		1.841
MP2/6-311G**	monomer	1.221	1.377		1.004	1.005				
MP2/6-311G(3df,2p)	monomer	1.219	1.370		1.002	1.002				
B3PW91/D95**	monomer	1.226	1.378		1.006	1.006				
	CF dimer, d	1.231	1.376		1.011	1.005			2.122	
	CF dimer, a	1.234	1.370		1.007	1.007				
	RF dimer	1.243	1.357	1.376	1.007	1.032	1.006	1.006		1.779
B3PW91/D95++**	monomer	1.226	1.377		1.007	1.007				
	CF dimer, d	1.231	1.374		1.011	1.006			2.153	
	CF dimer, a	1.234	1.369		1.007	1.007				
	RF dimer	1.242	1.356	1.375	1.007	1.031	1.007	1.007		1.795
Neutron diffraction	crystal	1.261	1.345		1.005	1.009			2.058	

for the  $\text{NH}_2$  groups involved in the H-bonds. The effects are larger for the **RF** than the **CF** dimers. Effects similar to those observed for **RF** were reported for acetic acid dimers<sup>8</sup> (which have a similar cyclic H-bonding structure), in agreement with experimental<sup>9</sup> observations. No similar experimental reports exist for urea dimers in the gas phase. These trends are consistent with reinforced polarization (opposite charge developing on alternate atoms) in  $\text{O}=\text{C}-\text{N}-\text{H}\cdots\text{O}$  in the ribbon dimer. They are also consistent with the resonance-assisted H-bonds proposed by Gilli.<sup>10</sup>

#### 4.5 Simulation of H-bonding effects with a uniform electric field .

From the above discussion, one sees that HF calculations favor planar monomers and dimers while MP2 favors nonplanarity. The DFT calculations tend to favor planar structures except for the **R** dimers. If one considers the interaction energies between planar monomers to form planar dimers, all the *ab initio* methods agree reasonably well, as does AM1. However, the interaction energy between optimized monomers and dimers includes a destabilizing contribution from the energy of planarization. One might reasonably expect the monomers to planarize upon polarization.

To test this hypothesis, we optimized the urea monomers in uniform electric fields up to 0.06 atomic units (electron/bohr) using the HF and MP2/D95\*\* models. The field strength in the crystal was estimated using HF/D95\*\* calculations for the cluster of 6 molecules (Figure 3.4) with the central molecule removed. The values obtained for the field strength in the positions of the atoms of the central molecule are from 0.017 to 0.023 au. Therefore, the molecule in the crystal is subject to external field of about 0.02 au.

The results for the monomer optimization in the external field are presented in Table 4.10. At HF level urea molecule planarizes at a field of 0.02 au and remains planar at higher fields. At MP2 level urea molecule becomes almost planar at 0.04 au (the planarization energy is  $< 0.1$  kcal/mol). However, increase in the field strength to 0.06 au drive H atoms in syn positions to O atom, which form N-H bonds orthogonal to the field direction, out of the molecular plane (planarization energy is 0.24 kcal/mol). Apparently, more sophisticated configurations of the electric field are necessary to simulate H-bonds in different directions.

To further investigate the possibility of simulating H-bonding effects with an electric field we performed geometry optimization of CH...O-bonded complexes H<sub>2</sub>O...HCN, H<sub>2</sub>O...HCCH, and H<sub>2</sub>O...HCH<sub>3</sub>, and compared the changes in C-H bond length with those in uniform electric field. GAMESS-UK was used, the numerical force constant matrix was calculated on each optimization step. The results are presented in Table 4.11. One can see, that C-H bonds in HCN and HCCH become longer upon H-bond formation, whereas in methane C-H bond involved in H-bonding becomes longer. This trend is well reproduced by a uniform electric field. Increasing field strength from 0 to 0.02 a.u. makes C-H bond in methane shorter, but a further increase elongates the bond again. Also, the electric field in the H-C direction stabilizes CH<sub>4</sub> molecule stronger, then in the C-H direction. The possible reason for this unusual behavior could be found in the polarity of C-H bond. In methane this bond has polarity C<sup>+</sup>H<sup>-</sup>, opposite to the one it has in acetylene C<sup>-</sup>H<sup>+</sup>, so that H-bonding (or weak external electric field) decrease its polarity, and the bond becomes more covalent. Unfortunately, the Mulliken charge does not capture this subtle effect: charges on H atoms in HCN, HCCH, and HCH<sub>3</sub> are: 0.22, 0.19, 0.14. However, integration of the electron density over the atomic

**Table 4.10.** Urea planarization in uniform electric field: F - field strength, a.u.;  $\Delta E_{\text{pl}}$  - planarization energy, kcal/mol;  $\mu_{\text{D}}$  - molecular dipole moment, D; OCNH, OCNH' - dihedrals,<sup>o</sup>;  $\Delta E$  - stabilisation energy in the field (the difference in total energy with and without the field), kcal; classical value  $m_{\text{D}}F$  is given for comparison, kcal/mol

Method	F	$\Delta E_{\text{pl}}$	OCNH	OCNH'	$\mu_{\text{D}}(\text{C}_2)$	$\mu_{\text{D}}(\text{C}_{2v})$	$\Delta E$	$\Delta_{\text{D}}F$
HF/D95**	0.00	1.29	12.6	151.0	4.01	4.70	0.00	-0.00
HF/D95**	0.01	0.21	12.0	164.3	5.39	5.61	-12.73	-13.86
HF/D95**	0.02	0.00	0.0	180.0	6.52	6.52	-27.70	-32.22
HF/D95**	0.04	0.00	0.0	180.0	8.35	8.35	-64.41	-82.54
HF/D95**	0.06	0.00	0.0	180.0	10.24	10.24	-110.27	-151.72
MP2/D95**	0.00	2.50	14.7	146.5	3.46	4.38	0.00	-0.00
MP2/D95**	0.01	0.87	17.1	158.4	4.44	5.37	-12.03	-13.26
MP2/D95**	0.02	0.24	16.8	169.1	6.24	6.36	-26.50	-31.43
MP2/D95**	0.04	0.07	15.9	178.3	8.39	8.38	-62.87	-82.80
MP2/D95**	0.06	0.24	22.4	178.3	10.54	10.47	-109.37	-155.27

basin (following Bader<sup>11</sup>) yields 0.21, 0.14, and -0.06. Based on C-H bond length, H<sub>2</sub>O creates the field of 0.018, 0.015, and 0.007 a.u. in the vicinity of H atoms in complexes with HCN, HCCH, and HCH<sub>3</sub> respectively. Values for the induced dipole moment and stabilization energy of the molecule in the external field of this strength are reasonably close to those obtained for H-bonded complexes (see Table 4.11). The decrease in the field strength is consistent with the increase of O...H distances from 2.08, to 2.24, to 2.90 Å in these complexes.



**Table 4.11.** HF/D95\*\* results on C-H bond lengths (Å) in H-bonded complex and a uniform electric field: F (a.u.): Mulliken charge on H atom, dipole moment (D), and stabilization energy (kcal/mol). For H-bonded complexes: molecular dipole moments  $\mu$  are obtained by subtraction of  $\mu(\text{H}_2\text{O})$  from the total dipole moment, interaction energies  $\Delta E$  are CP-corrected.

F	H-C	q(H)	$\mu$	$\Delta E$
H <sub>2</sub> O...HCN	1.0691	0.24	3.86*	-5.14
-0.0400	1.0544	0.06	1.07	21.22
-0.0100	1.0585	0.18	2.68	7.26
0.0000	1.0614	0.21	3.21	0.00
0.0100	1.0652	0.25	3.74	-8.57
0.0200	1.0699	0.28	4.27	-18.41
0.0500	1.0907	0.38	5.90	-56.02
H <sub>2</sub> O...HCCH	1.0643	0.16	0.56*	-1.20
-0.0500	1.0579	-0.03	-3.86	-23.60
-0.0400	1.0566	0.01	-3.07	-15.05
-0.0300	1.0561	0.05	-2.29	-8.44
-0.0200	1.0564	0.09	-1.52	-3.75
-0.0100	1.0576	0.13	-0.76	-0.94
-0.0050	1.0585	0.15	-0.38	-0.23
0.0000	1.0597	0.17	0.00	0.00
0.0050	1.0610	0.19	0.38	-0.23
0.0100	1.0626	0.20	0.76	-0.94
0.0200	1.0665	0.24	1.52	-3.75
0.0300	1.0715	0.27	2.29	-8.44
0.0400	1.0776	0.31	3.07	-15.05
0.0500	1.0852	0.34	3.86	-23.60
H <sub>2</sub> O...HCH <sub>3</sub>	1.0832	0.160	0.20*	-0.12
-0.0500	1.1160	-0.157	-1.79	-10.71
-0.0400	1.1057	-0.096	-1.40	-6.76
-0.0300	1.0977	-0.037	-1.03	-3.76
-0.0200	1.0916	0.019	-0.67	-1.66
-0.0150	1.0891	0.046	-0.50	-0.93
-0.0100	1.0871	0.073	-0.33	-0.41
-0.0075	1.0862	0.087	-0.24	-0.23
-0.0050	1.0854	0.100	-0.16	-0.10
-0.0025	1.0847	0.113	-0.08	-0.03
0.0000	1.0840	0.127	0.00	0.00
0.0025	1.0835	0.140	0.08	-0.03
0.0050	1.0830	0.153	0.16	-0.10
0.0075	1.0826	0.166	0.24	-0.23
0.0100	1.0822	0.179	0.32	-0.40
0.0200	1.0818	0.230	0.65	-1.61
0.0300	1.0824	0.281	0.97	-3.61
0.0400	1.0850	0.319	1.31	-6.47
0.0500	1.0875	0.383	1.61	-10.00

## 4.6 Heat of sublimation estimated from enthalpy of dimerization

The relative stabilities of the dimers are calculated to be the same:

**R>C>HB>SC>ST** by all *ab initio* methods used. If one compares enthalpy of the H-bond relative to the planar monomer, the results of different methods also agree (Table 4.8). One can try to estimate enthalpy of sublimation for urea crystal by adding *ab initio* values for enthalpy of dimerization for all the H-bonding dimers in the crystal. For tetragonal structure (Figure 3.4) at HF level one **CF** dimer (7.2 kcal/mol) and two **HF** dimers (4.0 kcal/mol) yield 15.2 kcal/mol, and at DFT level we get  $6.2+2\times 4.0=14.2$  kcal/mol. For orthogonal structure (Figure 3.5) at HF level one **RF** dimer (10.1 kcal/mol) and one **CF** dimer (7.2 kcal/mol) yield 17.3 kcal/mol and at DFT level we get  $11.2+6.2=17.4$  kcal/mol. As a result, the orthogonal structure turns out to be 2-3 kcal/mol more stable than the experimental tetragonal structure. Thus, the dimeric interactions are insufficient to explain the observed crystal structures. Rather, the crystal structure must be dictated by cooperative interactions involving several molecules, as it will be shown in Chapters 5 and 7.

## 4.7 Conclusions

The present calculations confirm the previous reports that the minima on the urea potential surface correspond to a nonplanar structure. However, increasing size of the basis set decrease the planarization energy so that after ZPVE the monomer is more stable in the planar conformation at HF/D95\*\*, B3PW91/D95+\*\*, MP2/6-311+G(3df,2p) and higher levels.

MP2/D95\*\* calculations predict the transition state between the  $C_2$  and  $C_s$  structures to be below the zero point vibration, which means that neither of them can be observed in the experiment.

The multiple minima found for the urea monomer complicate the calculations of urea dimers. HF and DFT calculations suggest that the dimers are planar or planarize with little distortion. The MP2 calculations predict the dimers to be nonplanar. However, the planarization energies for the dimers are similar to that of one monomer (not two). These results justify the use of planar geometry for ribbons and chains, considered in the next chapter.

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